



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C08F 220/56, 220/18, 220/06, 226/04, 8/00, D21H 17/33	A1	(11) International Publication Number: WO 00/43429 (43) International Publication Date: 27 July 2000 (27.07.00)
(21) International Application Number: PCT/US00/01615 (22) International Filing Date: 25 January 2000 (25.01.00) (30) Priority Data: 60/117,167 25 January 1999 (25.01.99) US 09/299,977 27 April 1999 (27.04.99) US (71) Applicant: KIMBERLY-CLARK WORLDWIDE, INC. [US/US]; 401 N. Lake Street, Neenah, WI 54956 (US). (72) Inventors: SHANNON, Thomas, Gerard; 1604 Meadowbreeze Circle, Neenah, WI 54956 (US). CLARAHAN, Daniel, Arthur; 1642 Wayside Road, Greenleaf, WI 54126 (US). GOULET, Mike, Thomas; 2305 West Seneca Drive, Appleton, WI 54914 (US). SCHROEDER, Wen, Zyo; 3120 West Capitol Drive, Appleton, WI 54914 (US). (74) Agents: CROFT, Gregory, E. et al.; Kimberly-Clark Worldwide, Inc., 401 N. Lake St., Neenah, WI 54956 (US).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: SYNTHETIC POLYMERS HAVING HYDROGEN BONDING CAPABILITY AND CONTAINING ALIPHATIC HYDRO-CARBON MOIETIES (57) Abstract <p>Synthetic polymers having hydrogen bonding capability and one or more aliphatic hydrocarbon moieties are capable of providing two distinct properties to paper products, such as tissues, which properties heretofore have been imparted through the use of at least two different molecules. The backbone of these synthetic polymers is based on modified vinyl polymers, such as polyvinyl alcohol, polyacrylamides and polyacrylic acids.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NI	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LJ	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

**SYNTHETIC POLYMERS HAVING HYDROGEN BONDING CAPABILITY AND
CONTAINING ALIPHATIC HYDROCARBON MOIETIES**

Background of the Invention

In the manufacture of paper products, such as facial tissue, bath tissue, paper towels, dinner napkins and the like, a wide variety of product properties are imparted to the final product through the use of chemical additives. Examples of such additives include softeners, debonders, wet strength agents, dry strength agents, sizing agents, opacifiers and the like. In many instances, more than one chemical additive is added to the product at some point in the manufacturing process. Unfortunately, there are instances where certain chemical additives may not be compatible with each other or may be detrimental to the efficiency of the papermaking process, such as can be the case with the effect of wet end chemicals on the downstream efficiency of creping adhesives.

Another limitation, which is associated with wet end chemical addition, is the limited availability of adequate bonding sites on the papermaking fibers to which the chemicals can attach themselves. Under such circumstances, more than one chemical functionality competes for the limited available bonding sites, oftentimes resulting in the insufficient retention of one or both chemicals on the fibers. For more complex chemical systems it may desirable to have two or more functional additives retained in a specified ratio and/or spatial arrangement relative to one another. Although the addition of chemicals in a pre-determined ratio is easily achieved, retention of these chemicals in a predictable ratio is difficult using wet end chemical addition because of site competition and other influencing factors. Another limitation of either wet end or topical chemical addition is the inability to predictably locate functional chemical moieties in proximity to each other on the fiber surface.

Therefore, there is a need for a means of applying more than one chemical functionality to a paper web that mitigates the limitations created by limited number of bonding sites and the unpredictable nature of chemical additive retention which limits the ability to retain functional groups in a specified ratio and/or spatial arrangement with respect to one another.

Summary of the Invention

In certain instances, two or more chemical functionalities can be combined into a single molecule, such that the combined molecule imparts at least two distinct

product properties to the final paper product that heretofore have been imparted through the use of two or more different molecules. More specifically, synthetic polymers, which are commonly used in the paper industry as dry strength resins, wet strength resins and retention aids, can be combined into a single molecule with modified aliphatic

5 hydrocarbons, which are commonly utilized, in conjunction with cationic moieties, as softeners, debonders, lubricants and sizing agents. The resulting molecule is a synthetic polymer having hydrogen bonding capability and an aliphatic hydrocarbon moiety which can provide several potential benefits, depending on the specific combination employed, including: (a) strength aids that soften; (b) softeners that do not reduce strength; (c) wet

10 strength with improved wet/dry strength ratio; (d) debonders with reduced linting and sloughing; (e) strength aids with controlled absorbency; and (g) retention aids that soften.

As used herein, "aliphatic hydrocarbon moieties" are functional groups derived from a broad group of organic compounds, including alkanes, alkenes, alkynes and cyclic aliphatic classifications. The aliphatic hydrocarbon moieties can be linear or branched,

15 saturated or unsaturated, substituted or non-substituted.

The synthetic polymers as described herein, have a portion of their structure derived from the polymerization of ethylenically unsaturated compounds which contain pendant groups that can form hydrogen bonds, ionic bonds or covalent bonds with cellulose molecules in fibers, thereby increasing interfiber bonding. They include

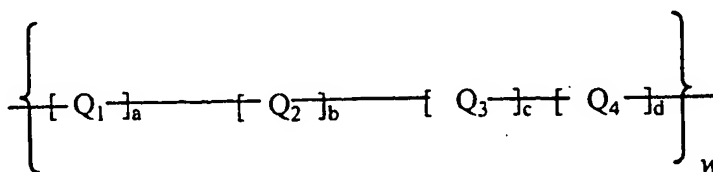
20 polyacrylamide, polyvinyl alcohol, polyacrylic acid, polymaleic anhydride, polymaleic acid, polyitaconic acid, cationic polyacrylamides, anionic polyacrylamides, and the like. The synthetic polymers as described herein may be water soluble, organic soluble or soluble in mixtures of water and water miscible organic compounds. Preferably they are water-soluble or water dispersible but this is not a necessity of the invention. Also included

25 within the definition are the salts of the above mentioned acidic polymers. Substances which can be combined with the acidic portion of the polymers to make the salts include the alkali metals such as K and Na usually added in form of their hydroxides, the aliphatic amines and alkanol amines, such salts and methods of preparing such salts being well known to those skilled in the art.

30 Depending upon the chemical and the desired impact on the paper sheet, the synthetic polymers of this invention may be applied to the paper web by any of the means known to those skilled in the art. Such means include wet end addition, spray addition on the wet web, as a creping chemical sprayed on the Yankee dryer, or as a post treatment addition, including spraying, printing or coating.

Hence in one aspect, the invention resides in a synthetic polymer having hydrogen bonding capability and containing one or more aliphatic hydrocarbon moieties, said synthetic polymer having the following structure:

5



where:

10 $a, b > 0$;

$c, d \geq 0$ such that $c+d > 0$;

$w \geq 1$;

Q_1 = a monomer unit or a block or graft copolymer containing a pendant group capable of forming hydrogen or covalent bonds with cellulose. Preferred pendant groups for hydrogen bonding are $-\text{CONH}_2$, $-\text{COOH}$, $-\text{COO}^- \text{M}^+$, $-\text{OH}$ and mixtures of said groups. Preferred pendant groups for covalent bonding are aldehydes and anhydrides. M^+ can be any suitable counter ion including Na^+ , K^+ , Ca^{+2} and the like.

20 Q_2 = a monomer unit or a block or graft copolymer containing a C_8 or higher linear or branched, saturated or unsaturated, substituted or unsubstituted aliphatic hydrocarbon moiety. Q_2 may take the form of $-\text{Z}_1-\text{Q}_2-\text{Z}_1'$ where Z_1 , Z_1' are any bridging radicals, the same or different, whose purpose is to provide incorporation into the polymer backbone and Q_2 is as defined previously;

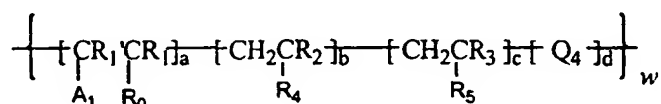
Q_3 = a monomer unit or a block or graft copolymer containing a charge functionality. Such charge functionality is preferably cationic but may be anionic or amphoteric; and

30 Q_4 = a monomer unit or a block or graft copolymer containing a hydrophilic moiety, which is desirable for making the material into a form suitable for papermaking. Q_4 may take the form of $-\text{Z}_2-\text{Q}_4-\text{Z}_2'$ where Z_2 , Z_2' are any bridging radicals, the same or different, whose purpose is to provide incorporation into the polymer backbone and Q_4 is as defined previously. Q_4 may be incorporated to offset the increased polymer hydrophobicity caused by introduction of the aliphatic hydrocarbon moieties. Examples of suitable Q_4 moieties are (but not limited to) the aliphatic polyether derivatives of the formula $-\{(\text{CR}_1\text{R}_2)_x\text{O}\}_y-\text{R}_3$, wherein R_1 , R_2 is H or

CH₃, x ≥ 2, y ≥ 1 and R₃ is any suitable terminal group including -CH₃, -H, -C₂H₅, -NH₂.

It should be appreciated that when the Q₃ or other charged moiety is present in the synthetic polymer, that a suitable counterion will be necessary. Such counterions may or may not be represented in the formulas. Where such counterions are not represented in the formula it should be understood that such an ion will exist. The specific counterion is not critical for the invention, such counterion is only necessary for providing charge balance. For cationically charged groups the most common anions are those of the halides and alkyl sulfates. For anionically charged groups on the polymer the most common counter ions will be those of the alkali and alkaline earth metals as well as ammonia and amine derivatives.

More specifically, the invention resides in a synthetic polymer having the following structure:



where:

 $w \geq 1;$
$$R_1, R_1', R_2, R_3 = \text{H, C}_{1-4} \text{ alkyl;}$$

20 $a, b > 0$;

$c, d \geq 0$ such that $c + d > 0$:

Q_4 = a monomer unit or a block or graft copolymer containing a hydrophilic moiety, which is desirable for making the material into a form suitable for papermaking. Q_4 may take the form of $-Z_2-Q_4-Z_2'$ where Z_2, Z_2' are any bridging radicals, the same or different, whose purpose is to provide incorporation into the polymer backbone and Q_4 is as defined previously. Q_4 may be incorporated to offset the increased polymer hydrophobicity caused by introduction of the aliphatic hydrocarbon moieties. Examples of suitable Q_4 moieties are (but is not limited to) the aliphatic polyether derivatives of the formula $\text{---}[(CR_1R_2)_xO]_y\text{---}R_3$, wherein R_1, R_2 is H or CH_3 , $x \geq 2$, $y \geq 1$ and R_3 is any suitable terminal group including $-CH_3$, $-H$, $-C_2H_5$, $-NH_2$;

R_0 = any group capable of forming hydrogen or covalent bonds with cellulose. Preferred are $-\text{CONH}_2$, $-\text{COOH}$, COO^-M^+ , $-\text{OH}$, $-\text{CONHCHOHCHO}$ and mixtures of said groups;

A_1 = $-\text{H}$, $-\text{COOH}$;

5 R_4 = $Z - R_6 - Y$ radical where:

Z = aryl, $-\text{CH}_2-$, $-\text{COO}-$, $-\text{CONR}'-$, $-\text{O}-$, $-\text{S}-$, $-\text{OSO}_2\text{O}-$, $-\text{CONHCO}-$, $-\text{CONHCHOHCHOO}-$ or any other radical capable of bridging the R_6 group to the vinyl backbone portion of the molecule. ($R' = \text{H}$, alkyl);

10 R_6 = any linear or branched, saturated or unsaturated, substituted or non-substituted aliphatic hydrocarbon;

Y = H , $-\text{N}^+\text{R}_7\text{R}_8\text{R}_9$, $-\text{NR}_7\text{R}_8$, where R_7 , R_8 , R_9 are same or different and are H or C_{1-30} linear or branched, saturated or unsaturated aliphatic hydrocarbons;

At least one of R_6 , R_7 , R_8 , R_9 must be an aliphatic, linear or branched, substituted or non-substituted, hydrocarbon of chain length 8 or higher;

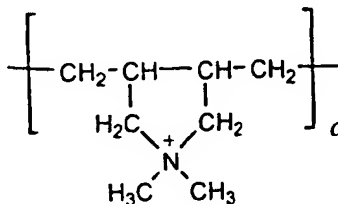
15 R_5 = $Z_2 - R_{10} - W$;

Z_2 = aryl, $-\text{CH}_2-$, $-\text{COO}-$, $-\text{CONH}-$, $-\text{O}-$, $-\text{S}-$, $-\text{OSO}_2\text{O}-$, any radical capable of bridging the R_{10} group to the vinyl backbone portion of the molecule;

R_{10} = any linear or branched, aliphatic or aromatic hydrocarbon of 2 or more carbons, preferably $-(\text{CH}_2\text{CH}_2)-$, $-\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_2-$; and

20 W = $-\text{N}^+\text{R}_{11}\text{R}_{12}\text{R}_{13}$ where R_{11} , R_{12} , R_{13} is a C_{1-4} alkyl group.

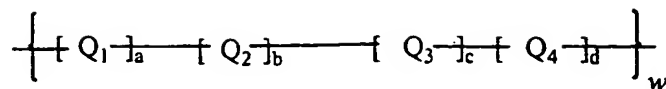
$-\text{[CH}_2\text{CR}_3\text{R}_5\text{]}_c-$ may also be the residue formed by co-polymerization with dimethyldiallyl ammonium chloride. In this case the charge-containing residue $-\text{[CH}_2\text{CR}_3\text{R}_5\text{]}_c-$ will be the form of monomers with repeat units of structure:



25

In another aspect, the invention resides in a paper sheet, such as a tissue sheet, comprising a synthetic polymer having hydrogen bonding capability and containing an aliphatic hydrocarbon moiety, said polymer having the following structure:

30



where:

5 a, b > 0;

c, d ≥ 0;

w ≥ 1;

10 Q₁ = a monomer unit or a block or graft copolymer containing a pendant group capable of forming hydrogen or covalent bonds with cellulose. Preferred pendant groups for hydrogen bonding are —CONH₂, —COOH, —COO[−] M⁺, —OH and mixtures of said groups. Preferred pendant groups for covalent bonding are aldehydes and anhydrides. M⁺ can be any suitable counter ion including Na⁺, K⁺, Ca⁺² and the like;

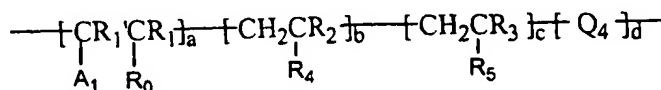
15 Q₂ = a monomer unit or a block or graft copolymer containing a C₈ or higher linear or branched, saturated or unsaturated, substituted or unsubstituted aliphatic hydrocarbon moiety. Q₂ may take the form of —Z₁—Q₂—Z₁'— where Z₁, Z₁' are any bridging radicals, the same or different, whose purpose is to provide incorporation into the polymer backbone and Q₂ is as defined previously;

20 Q₃ = a monomer unit or a block or graft copolymer containing a charge functionality. Such charge functionality is preferably cationic but may be anionic or amphoteric; and

25 Q₄ = a monomer unit or a block or graft copolymer containing a hydrophilic moiety, which is desirable for making the material into a form suitable for papermaking. Q₄ may take the form of —Z₂—Q₄—Z₂'— where Z₂, Z₂' are any bridging radicals, the same or different, whose purpose is to provide incorporation into the polymer backbone and Q₄ is as defined previously. Q₄ may be incorporated to offset the increased polymer hydrophobicity caused by introduction of the aliphatic hydrocarbon moieties. Examples of suitable Q₄ moieties are (but is not limited to) the aliphatic polyether derivatives of the formula —[(CR₁R₂)_xO]_y—R₃, wherein R₁, R₂ is H or CH₃, x ≥ 2, y ≥ 1 and R₃ is any suitable terminal group including —CH₃, —H, —C₂H₅, —NH₂.

30

More specifically, the invention resides in a paper sheet, such as a tissue sheet, comprising a synthetic polymer having hydrogen bonding capability and containing an aliphatic hydrocarbon moiety, said polymer having the following structure:



5

where:

$w \geq 1$;

$R_1, R_1', R_2, R_3 = \text{H, C}_{1-4} \text{ alkyl};$

10 $a, b > 0$;

$c, d \geq 0$;

$\text{Q}_4 =$ a monomer unit or a block or graft copolymer containing a hydrophilic moiety, which

is desirable for making the material into a form suitable for papermaking. Q_4 may

take the form of $-\text{Z}_2-\text{Q}_4-\text{Z}_2'-$ where Z_2, Z_2' are any bridging radicals, the same or

15

different, whose purpose is to provide incorporation into the polymer backbone

and Q_4 is as defined previously. Q_4 may be incorporated to offset the increased

polymer hydrophobicity caused by introduction of the aliphatic hydrocarbon

moieties. Examples of suitable Q_4 moieties are (but is not limited to) the aliphatic

polyether derivatives of the formula $-\text{[(CR}_1\text{R}_2)_x\text{O}]_y-\text{R}_3$, wherein R_1, R_2 is H or

20

CH_3 , $x \geq 2$, $y \geq 1$ and R_3 is any suitable terminal group including $-\text{CH}_3$, $-\text{H}$, $-\text{C}_2\text{H}_5$, $-\text{NH}_2$;

$\text{R}_0 =$ any group capable of forming hydrogen or covalent bonds with cellulose. Preferred

are $-\text{CONH}_2$, $-\text{COOH}$, COO^-M^+ , $-\text{OH}$, $-\text{CONHCHOHCHO}$, and anhydride including

mixtures of said groups;

25 $\text{A}_1 = \text{H, COOH};$

$\text{R}_4 = \text{Z} - \text{R}_6 - \text{Y}$ radical where:

$\text{Z} =$ aryl, $-\text{CH}_2-$, $-\text{COO}-$, $-\text{CONR}'-$, $-\text{O}-$, $-\text{S}-$, $-\text{OSO}_2\text{O}-$, $-\text{CONHCO}-$, $-\text{CONHCHOHCHOO}-$ or any radical capable of bridging the R_6 group to the vinyl

backbone portion of the molecule. ($\text{R}' = -\text{H, alkyl}$);

30 $\text{R}_6 =$ any aliphatic, linear or branched, saturated or unsaturated, substituted or non-substituted hydrocarbon;

$\text{Y} = -\text{H}$, $-\text{N}^+\text{R}_7\text{R}_8\text{R}_9$, $-\text{NR}_7\text{R}_8$, where $\text{R}_7, \text{R}_8, \text{R}_9$ are same or different and are H or C_{1-30} linear or branched, saturated or unsaturated aliphatic hydrocarbons;

At least one of R_6 , R_7 , R_8 , R_9 must be an aliphatic, linear or branched, substituted or non-substituted, hydrocarbon of chain length 8 or higher;

$R_5 = Z_2-R_{10}-W$;

$Z_2 =$ aryl, $-\text{CH}_2-$, $-\text{COO}-$, $-\text{CONH}-$, $-\text{O}-$, $-\text{S}-$, $-\text{OSO}_2\text{O}-$ or any radical capable of bridging the

5 R_{10} group to the vinyl backbone portion of the molecule;

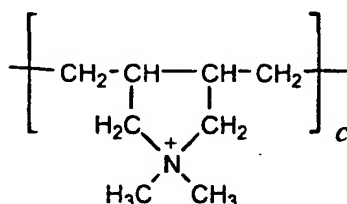
$R_{10} =$ any linear or branched, aliphatic or aromatic hydrocarbon of 2 or more carbons, preferably $-(\text{CH}_2\text{CH}_2)-$, $-\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_2-$; and

$W = -\text{N}^+\text{R}_{11}\text{R}_{12}\text{R}_{13}$ where R_{11} , R_{12} , R_{13} is a C_{1-4} alkyl group.

$-\text{[CH}_2\text{CR}_3\text{R}_5]\text{c}-$ may also be the residue formed by co-polymerization with

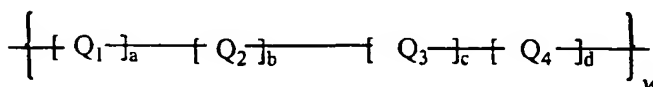
10 dimethyldiallyl ammonium chloride. In this case the charge-containing residue

$-\text{[CH}_2\text{CR}_3\text{R}_5]\text{c}-$ will be the form of monomers with repeat units of structure:



15 In another aspect, the invention resides in a method of making a paper sheet, such as a tissue sheet, comprising the steps of: (a) forming an aqueous suspension of papermaking fibers; (b) depositing the aqueous suspension of papermaking fibers onto a forming fabric to form a web; and (c) dewatering and drying the web to form a paper sheet, wherein a synthetic polymeric additive is added to the aqueous suspension of

20 fibers or to the web, said polymeric additive having the following structure:



where:

25 $a, b > 0$;

$c, d \geq 0$;

$w \geq 1$;

$\text{Q}_1 =$ a monomer unit or a block or graft copolymer containing a pendant group capable of forming hydrogen or covalent bonds with cellulose. Preferred pendant groups for hydrogen bonding are $-\text{CONH}_2$, $-\text{COOH}$, $-\text{COO}^- \text{M}$, $-\text{OH}$ and mixtures of

30 said groups. Preferred pendant groups for covalent bonding are aldehydes and

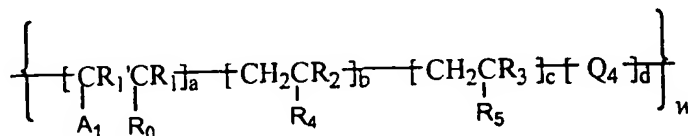
anhydrides. M⁺ can be any suitable counter ion including Na⁺, K⁺, Ca⁺² and the like;

Q₂ = a monomer unit or a block or graft copolymer containing a C₈ or higher linear or branched, saturated or unsaturated, substituted or unsubstituted aliphatic hydrocarbon moiety. Q₂ may take the form of -Z₁-Q₂-Z₁'- where Z₁, Z₁' are any bridging radicals, the same or different, whose purpose is to provide incorporation into the polymer backbone and Q₂ is as defined previously;

Q₃ = a monomer unit or a block or graft copolymer containing a charge functionality. Such charge functionality is preferably cationic but may be anionic or amphoteric; and

Q₄ = a monomer unit or a block or graft copolymer containing a hydrophilic moiety, which is desirable for making the material into a form suitable for papermaking. Q₄ may take the form of -Z₂-Q₄-Z₂'- where Z₂, Z₂' are any bridging radicals, the same or different, whose purpose is to provide incorporation into the polymer backbone and Q₄ is as defined previously. Q₄ may be incorporated to offset the increased polymer hydrophobicity caused by introduction of the aliphatic hydrocarbon moieties. Examples of suitable Q₄ moieties are (but is not limited to) the aliphatic polyether derivatives of the formula —[(CR₁R₂)_xO]_y—R₃, wherein R₁, R₂ is -H or -CH₃, x ≥ 2, y ≥ 1 and R₃ is any suitable terminal group including -CH₃, -H, -C₂H₅, -NH₂.

More specifically, the invention resides in a method of making a paper sheet, such as a tissue sheet, comprising the steps of: (a) forming an aqueous suspension of papermaking fibers; (b) depositing the aqueous suspension of papermaking fibers onto a forming fabric to form a web; and (c) dewatering and drying the web to form a paper sheet, wherein a synthetic polymeric additive is added to the aqueous suspension of fibers or to the web, said polymeric additive having the following structure:



where:

w ≥ 1;

R₁, R₁', R₂, R₃ = H, C₁₋₄ alkyl;

a, b > 0;

c,d \geq 0;

5 Q_4 = a monomer unit or a block or graft copolymer containing a hydrophilic moiety, which is desirable for making the material into a form suitable for papermaking. Q_4 may take the form of $-Z_2-Q_4-Z_2'$ where Z_2, Z_2' are any bridging radicals, the same or different, whose purpose is to provide incorporation into the polymer backbone and Q_4 is as defined previously. Q_4 may be incorporated to offset the increased polymer hydrophobicity caused by introduction of the aliphatic hydrocarbon moieties. Examples of suitable Q_4 moieties are (but is not limited to) the aliphatic polyether derivatives of the formula $-(CR_1R_2)_xO)_y-R_3$, wherein R_1, R_2 is H or CH_3 , $x \geq 2$, $y \geq 1$ and R_3 is any suitable terminal group including $-CH_3$, $-H$, $-C_2H_5$, $-NH_2$;

R_0 = any group capable of forming hydrogen or covalent bonds with cellulose. Preferred are $-CONH_2$, $COOH$, COO^- , $-OH$, $CONHCHOHCHO$, and anhydride including mixtures of said groups;

15 A_1 = $-H$, $-COOH$;

R_4 = $Z - R_6 - Y$ radical where:

Z = aryl, $-CH_2-$, $-COO-$, $-CONR'$, $-O-$, $-S-$, $-OSO_2O-$, $-CONHCO-$, $-CONHCHOHCHOO-$ or any radical capable of bridging the R_6 group to the vinyl backbone portion of the molecule. ($R' = H$, alkyl);

20 R_6 = any aliphatic, linear or branched, saturated or unsaturated, substituted or non-substituted hydrocarbon;

Y = H , $-N^+R_{11}, R_{12}, R_{13}$, $-NR_7R_8$, where R_7, R_8, R_9 are same or different and are H or C_{1-30} linear or branched, saturated or unsaturated aliphatic hydrocarbons;

At least one of R_6, R_7, R_8, R_9 must be an aliphatic, linear or branched, substituted or non-substituted, hydrocarbon of chain length 8 or higher;

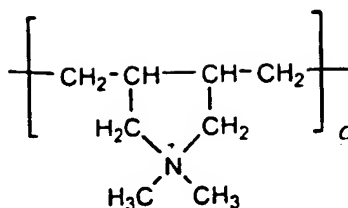
25 R_5 = $Z_2-R_{10}-W$;

Z_2 = aryl, $-CH_2-$, $-COO-$, $-CONH-$, $-O-$, $-S-$, $-OSO_2O-$ or any radical capable of bridging the R_{10} group to the vinyl backbone portion of the molecule;

R_{10} = any linear or branched, aliphatic or aromatic hydrocarbon of 2 or more carbons, preferably $-(CH_2CH_2)-$, $-C(CH_3)_2CH_2CH_2-$; and

30 W = $-N^+R_{11}, R_{12}, R_{13}$ where R_{11}, R_{12}, R_{13} is a C_{1-4} alkyl group.

$-[CH_2CR_3R_5]_c-$ may also be the residue formed by co-polymerization with dimethyldiallyl ammonium chloride. In this case the charge-containing residue $-[CH_2CR_3R_5]_c-$ will be the form of monomers with repeat units of structure:



5 The amount of the synthetic polymeric additive added to the fibers or the tissue web can be from about 0.02 to about 4 weight percent, on a dry fiber basis, more specifically from about 0.05 to about 2 weight percent, and still more specifically from about 0.1 to about 1 weight percent. The synthetic polymer can be added to the fibers or web at any point in the process, but it can be particularly advantageous to add the synthetic polymer to the fibers while the fibers are suspended in water.

10

Detailed Description of the Invention

To further describe the invention, examples of the synthesis of some of the various chemical species are given below.

15

First with regard to the synthetic polymers, they can be made via free radical polymerization of vinyl monomers of the form:



20

where R_1 , R_2 , R_3 , R_4 may be H, halogen, alkyl, functional alkyl, aryl, functional aryl. For papermaking the polyacrylamides ($\text{R}_4 = \text{---CONH}_2$), polyvinyl alcohols ($\text{R}_4 = \text{---OH}$), and polyacrylates ($\text{R}_4 = \text{---COOR}'$, $\text{R}' = \text{H, Me}$) are the most widely used.

25

Of the modified vinyl synthetic polymers, polyacrylamides (PAMs) are used as dry strength additives in addition to their widespread use as drainage and retention aids. They are water-soluble polymers containing primary amide groups that can form hydrogen bonds with cellulose molecules in fibers thereby increasing interfiber bonding. They are synthesized by the free radical polymerization of acrylamide as shown in Figure 1.

30



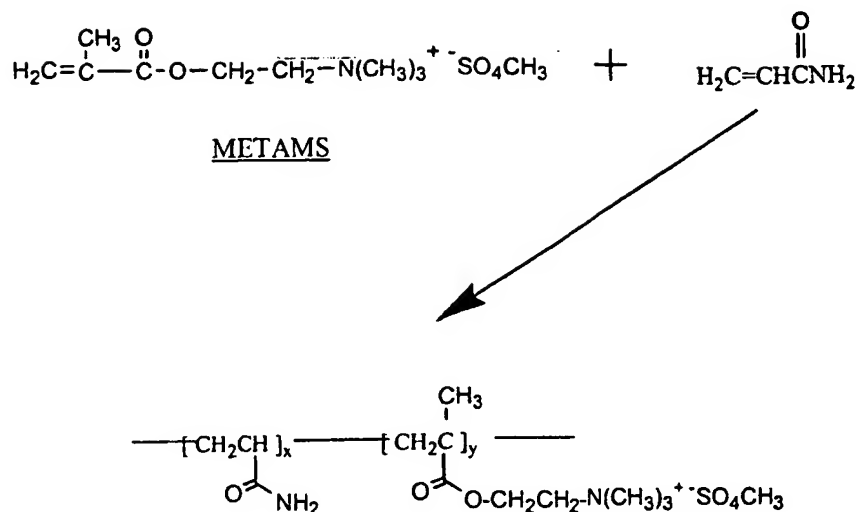
Figure 1

5 (PAMs) per se are nonionic materials and have very little attraction to papermaking fibers. Therefore it is necessary to incorporate charged groups into the polymer structure to make it useful for papermaking. Both anionic and cationic polyacrylamides are known in the art.

10 Anionic polyacrylamides can be produced by (1) the copolymerization of acrylamide with acrylic acid or the (2) hydrolysis of some of the amide groups on the polyacrylamide chain. The resultant polymer will contain a mixture of acrylamide and acrylic acid groups. Anionic polyacrylamides were first produced in the 1950's via copolymerization of acrylamide with acrylic acid. The acrylic acid groups introduce an ionizable carboxyl group on the polymer backbone. Ionization of these carboxyl groups is
15 highly pH dependent, where above pH 7 essentially 100% of the carboxyl groups are ionized. Since anionic polyacrylamides are negatively charged they are not directly attracted to the like-charged cellulose papermaking fibers. A cationic substance such as alum must be used in conjunction with them to promote their retention.

To avoid the need for a cationic promoter, another approach is to incorporate
20 cationic groups directly into the polymer backbone. Having been commercially produced since the late 1960's, these cationically charged polyacrylamides are the most common form of dry strength PAM's. Cationic polyacrylamides are produced by copolymerization of acrylamide with cationic monomers or by modification of some of the amide groups. Typical cationic monomers include: (1) methacryloyloxyethyl trimethyl ammonium
25 methosulfate (METAMS); (2) dimethyldiallyl ammonium chloride (DMAAC); (3) 3-acryloamido-3-methyl butyl trimethyl ammonium chloride (AMBTAC); (4) trimethylamino methacrylate; and (5) vinyl benzyl trimethyl ammonium chloride (VBTAC). A typical reaction for co-polymerization with METAMS is illustrated in Figure 2.

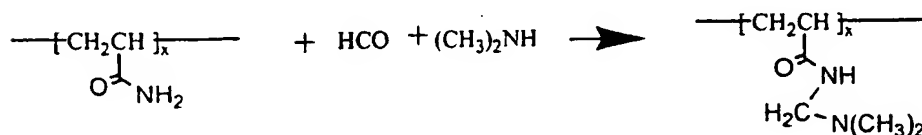
30

**Figure 2**

5

Production of cationic polyacrylamides by the modification of the amide groups of PAMs is most often accomplished via the Mannich reaction as illustrated in Figure 3. Generally cationic polyacrylamides synthesized in this manner will contain from about 5 to about 70 mole percent cationic groups.

10

**Figure 3**

15

Generally dry strength PAMs are supplied as ready to use aqueous solutions or as water-soluble powders which must be dissolved prior to use. They may be added to thin or thick stock at a point of good mixing for best results. Addition rates of 0.1% to 0.5% of dry fiber typically give best results. High addition rates may cause over-cationization of the furnish and reduce the effectiveness of other additives.

20

When used as dry strength additives usually around 10 mole % of the monomers will contain charged groups. Unlike the anionic PAMs, cationic PAMs can be effectively charged across the entire pH range. Typical molecular weights (Mw) for cationic PAM dry strength aids are in the range of 100,000 to 500,000. The molecular weight is important

so as to be low enough to not bridge between particles and cause flocculation, and yet high enough to retard migration of the polymer into the pores of the fibers. Such migration would cause a reduction in dry strength activity.

When used as retention aids a broader range of molecular weights and charge densities may be employed. Key characteristics of polyacrylamide retention aids include the molecular weight, the type of charge, the charge density and the delivery form. For the average molecular weight, the range can be: low (1,000 - 100,000); medium (100,000 - 1,000,000); high (1,000,000 - 5,000,000); very high (>5,000,000). The charge type can be nonionic, cationic, anionic or amphoteric. The charge density can be: low (1 - 10%); medium (10 - 40%); high (40 - 80%); or very high (80 - 100%). The delivery form can be an emulsion, an aqueous solution or a dry solid.

High molecular weight/ low charge density flocculants are used most often for retention of fine particles in high shear and turbulence environments. Low Mw, high charge density products are used for their charge modifying capabilities and for retention in low shear environments.

There are several envisioned pathways in which synthetic polymers containing hydrogen bonding groups and aliphatic hydrocarbons can be combined onto a single molecule for purposes of this invention. These include, but are not limited to: (1) block copolymerization and/or grafting ; (2) direct monomer incorporation ; and (3) derivatization of functional groups on the polymer backbone. Each of these methods is described below.-Since these materials maintain their bonding and/or charge characteristics they would be expected to maintain their dry strength and or retention capabilities as well as provide for materials with enhanced tactile properties due to introduction of the aliphatic hydrocarbon moieties.

The molar and weight ratios of the various functional groups on the polymer will largely depend on the specific application of the material and is not a critical aspect of the invention. However, the portion of the synthetic polymer [Q₁] capable of forming hydrogen, covalent and ionic bonds can constitute from about 10 to about 90 weight percent of the total polymer, more specifically from about 20 to about 80 weight percent of the total polymer and still more specifically from about 30 to about 70 weight percent of the total polymer. The aliphatic hydrocarbon portion [Q₂] of the synthetic polymer can constitute from about 10 to about 90 weight percent of the synthetic polymer, more specifically from about 20 to about 80 weight percent of the synthetic polymer and still more specifically from about 30 to about 70 weight percent of the synthetic polymer. The charge containing portion [Q₃] of the synthetic polymer can be comprised of monomer units constituting from 0 to about 80 mole percent of the total monomer units in the

synthetic polymer, more specifically from 0 to about 30 mole percent and still more specifically from about 5 to about 15 mole percent. The [Q₄] functionality will be comprised of monomer units constituting from 0 to about 80 mole percent of the total monomer units in the synthetic polymer, more specifically from 0 to about 40 mole percent and still more specifically from 0 to about 20 mole percent.

Likewise the molecular weight of the synthetic polymers of the present invention will largely depend on the specific application of the material and is not overly critical to the invention. The weight average molecular weight range can be from about 1,000 to about 5,000,000, more specifically from about 10,000 to about 2,000,000 and still more specifically from about 20,000 to about 1,000,000. Where these polymers are added for dry strength it is important that the molecular weight of the polymer be low enough so as to not bridge between particles and cause flocculation, and yet high enough so as to retard migration of the polymer into the pores of the fibers. These materials can have weight average molecular weights in the range of from about 5,000 to about 1,000,000, more specifically from about 10,000 to about 1,000,000 and still more specifically from about 20,000 to about 600,000.

Block copolymerization and/or grafting.

In this aspect of the invention one or more of the [Q]_i elements of the polymer exists as a block or graft copolymer on the vinyl backbone. For example, if the aliphatic hydrocarbon portion of the modified vinyl polymer was incorporated in such a manner, the aliphatic hydrocarbon portion would exist as a block copolymer of polyethylene, polypropylene, isobutylene, polytetrafluoroethylene, or any other linear or branched, saturated or unsaturated, substituted or non-substituted hydrocarbon, such co-polymer incorporated either as block or graft onto the vinyl backbone. Generally the aliphatic hydrocarbon blocks would be built as a result of the free radical polymerization of the corresponding ethylenically unsaturated monomers including, ethylene, propylene, perfluoroethylene, isobutylene and the like including mixtures of said monomers. These synthetic polymers are distinguished from those of the direct monomer incorporation in that the aliphatic hydrocarbon portion of the molecule would be incorporated linearly within the polymer chain rather than in a pendant fashion. Although the above example and the example in figure 4 are specific to the aliphatic hydrocarbon moiety incorporated via this approach it should be appreciated that any of the synthetic polymer elements or combination of the synthetic polymer elements Q₁, Q₂, Q₃, Q₄ could be incorporated via this approach. Note that where a polyacrylamide is employed that these polymers

maintain pendant amide functionality and are therefore capable of being glyoxylated to form materials possessing temporary wet strength. A general example of preparing such a material is shown in Figure 4.

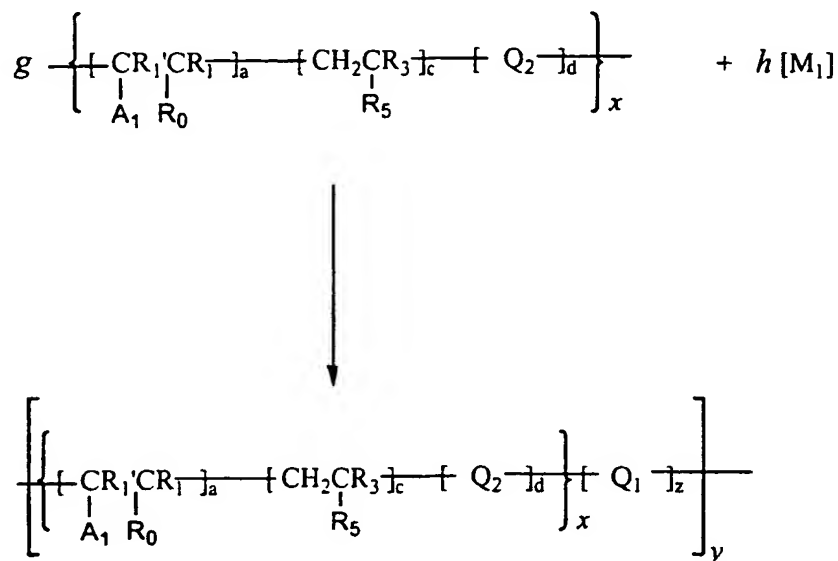


Figure 4

where:

$\text{R}_1, \text{R}_3, \text{R}_1' = \text{H}, \text{C}_{1-4} \text{ alkyl}$

10 $g, h, x \geq 1$

$x * y = g$

$b * y = h$

$a, b > 0$

$c, d \geq 0$

15 $\text{R}_0 =$ any group capable of forming hydrogen or covalent bonds with cellulose. Preferred are $-\text{CONH}_2$, COOH , COO^- , $-\text{OH}$, CONHCHOHCHO , and anhydride including mixtures of said groups;

$\text{A}_1 = \text{H}, \text{COOH}$

20 $\text{M}_1 =$ an unsaturated vinyl monomer unit capable of being polymerized into a polymer containing a C_8 or higher linear or branched, saturated or unsaturated, substituted or unsubstituted aliphatic hydrocarbon moiety. Alternatively M_1 could be an oligomer or polymer of such an unsaturated vinyl monomer.

$\text{Q}_2 =$ a block copolymer which is or contains a C_8 or higher linear or branched, saturated or unsaturated, substituted or unsubstituted aliphatic hydrocarbon moiety.

Q_4 = a monomer unit or a block or graft copolymer containing a hydrophilic moiety, which is desirable for making the material into a form suitable for papermaking. Q_4 may take the form of $-Z_2-Q_4-Z_2'$ where Z_2, Z_2' are any bridging radicals, the same or different, whose purpose is to provide incorporation into the polymer backbone and Q_4 is as defined previously. Q_4 may be incorporated to offset the increased polymer hydrophobicity caused by introduction of the aliphatic hydrocarbon moieties. Examples of suitable Q_4 moieties are (but is not limited to) the aliphatic polyether derivatives of the formula $-(CR_1R_2)_xO)_y-R_3$, wherein R_1, R_2 is H or CH_3 , $x \geq 2$, $y \geq 1$ and R_3 is any suitable terminal group including $-CH_3$, $-H$, $-C_2H_5$, $-NH_2$

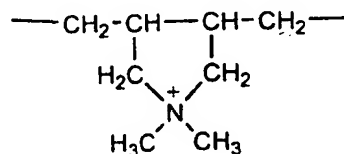
$R_5 = Z_2-R_{10}-W$

$Z_2 =$ Aryl, CH_2 , COO^- , $CONH^-$, $-O^-$, $-S^-$, $-OSO_2O^-$, any radical capable of bridging the R_{10} group to the vinyl backbone portion of the molecule.

$R_{10} =$ any linear or branched, aliphatic or aromatic hydrocarbon of 2 or more carbons, preferably $-(CH_2CH_2)-$, $-C(CH_3)_2CH_2CH_2-$

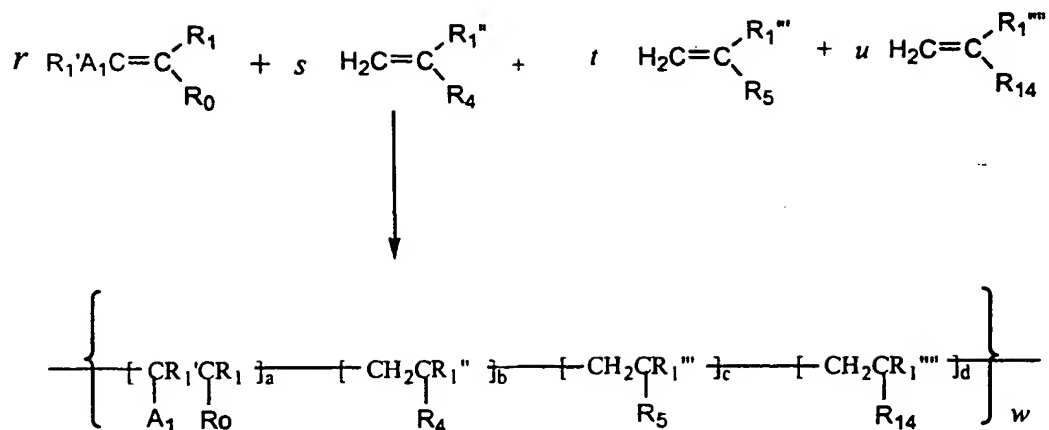
$W = -N^+R_{11}R_{12}R_{13}$, $NR_{11}R_{12}$, where R_{11}, R_{12}, R_{13} is a C_{1-4} alkyl group.

R_5 may also be the residue formed by co-polymerization with dimethyldiallyl ammonium chloride. In this case the residue will be the form of monomers with repeat units of structure:



Direct monomer incorporation.

Incorporation of the aliphatic moieties can be accomplished via copolymerization with vinyl type monomers containing aliphatic groups. Almost any vinyl type monomer containing a pendant aliphatic hydrocarbon can be co-polymerized with acrylamide or a similar vinyl monomer containing a pendant hydrogen-bonding moiety to be incorporated into the polymer backbone. Generically the synthesis can be described in Figure 5.

**Figure 5**

where:

- 5 $R_1, R_1', R_1'', R_1''', R_1'''' = H, C_{1-4} \text{ alkyl};$
 $a, b \geq 1;$
 $c, d \geq 0;$
 $w \geq 1;$
 $r, s \geq 1;$
- 10 $t, u \geq 0;$
 $a \cdot w = r;$
 $b \cdot w = s;$
 $c \cdot w = t;$
 $d \cdot w = u;$
- 15 $R_0 =$ any group capable of forming hydrogen or covalent bonds with cellulose. Preferred are $-\text{CONH}_2, \text{COOH}, \text{COO}^-, -\text{OH}, \text{CONHCHOHCHO},$ and anhydride including mixtures of said groups;
 $A_1 = H, \text{COOH};$
 $R_4 = Z - R_6 - Y$ radical where:
- 20 $Z =$ Aryl, $\text{CH}_2, \text{COO}^-, \text{CONH}-, -\text{O}-, -\text{S}-, -\text{OSO}_2\text{O}-, -\text{CONHCO}-, \text{CONHCHOHCHOO}-,$ any radical capable of bridging the R_6 group to the vinyl backbone portion of the molecule;
 $Y = H, -\text{N}+\text{R}_7\text{R}_8\text{R}_9, -\text{NR}_7\text{R}_8,$ where R_7, R_8, R_9 are same or different and are H or C_{1-30} aliphatic hydrocarbons;
- 25 $R_5 =$ any aliphatic, linear or branched, saturated or unsaturated, substituted or non-substituted hydrocarbon;

R_{14} = a moiety necessary for making the material into a form suitable for papermaking.

R_{14} may take the form of $-Z_1-R_{14}$ where Z_1 is any bridging radical whose purpose is to provide incorporation into the polymer backbone and R_{14} is as defined

previously. R_{14} may be incorporated to offset the increased polymer

hydrophobicity caused by introduction of the aliphatic hydrocarbon moieties.

Examples of suitable R_{14} moieties are (but is not limited to) the aliphatic polyether.

derivatives of the formula $—[(CR_1R_2)_xO]_y—R_{15}$, wherein R_1 , R_2 is H or CH_3 , $x \geq 2$, y

≥ 1 and R_{15} is any suitable terminal group including $-CH_3$, $-H$, $-C_2H_5$, $-NH_2$, and the like; and

- 10 At least one of R_6 , R_7 , R_8 , R_9 must be a C_8 or higher linear or branched, saturated or unsaturated, substituted or non-substituted, aliphatic hydrocarbon.

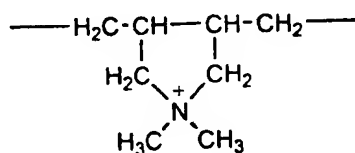
More specifically, $R_5 = Z_2-R_{10}-W$, where:

$Z_2 =$ Aryl, CH_2 , $COO-$, $CONH-$, $-O-$, $-S-$, $-OSO_2O-$, any radical capable of bridging
15 the R_{10} group to the vinyl backbone portion of the molecule;

$R_{10} =$ any linear or branched, aliphatic or aromatic hydrocarbon of 2 or more
carbons, preferably $-(CH_2CH_2)-$, $-C(CH_3)_2CH_2CH_2-$; and

$W = -N^+R_{11}, R_{12}, R_{13}$ where R_{11} , R_{12} , R_{13} is a C_{1-4} alkyl group.

- 20 R_5 can also be the residue formed by co-polymerization with dimethyldiallyl ammonium chloride. In this case the residue will be the form of monomers with repeat units of structure:



A specific example of the synthesis is shown in Figure 6.

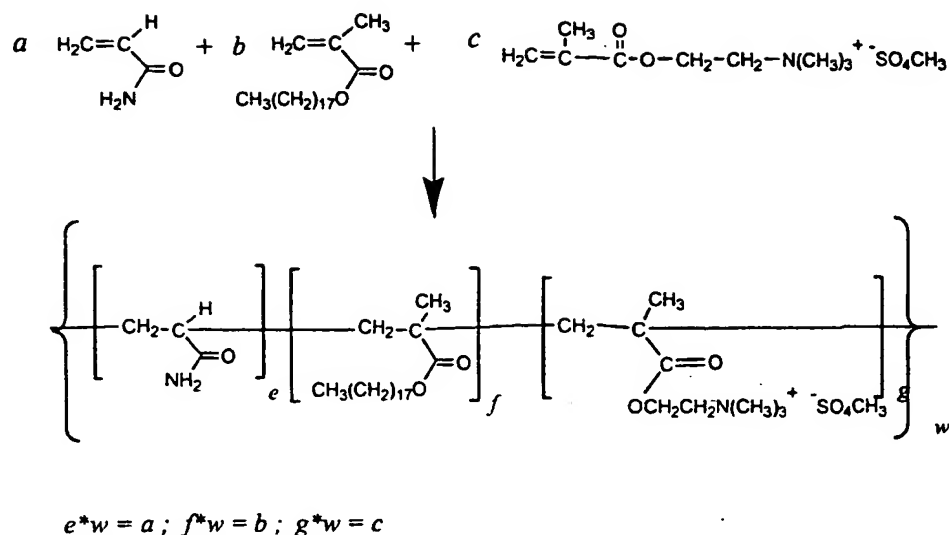


Figure 6

Long chain acrylates, including octadecyl acrylate, octadecyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, dodecyl acrylate, dodecyl methacrylate, tridecyl acrylate, tridecyl methacrylate, lauryl acrylate, lauryl methacrylate and the like including mixtures of said monomers are known commercially available materials and are all suitable for incorporation of the aliphatic hydrocarbon moiety.

Also known are various vinyl ethers dodecyl vinyl ether, tridecyl vinyl ether, tetradecyl vinyl ether, pentadecyl vinyl ether, hexadecyl vinyl ether, and esters such as those derived from aliphatic alcohols and α,β -ethylenic unsaturated carboxylic acids including vinyl neodecanoate, vinyl neononaoate, vinyl stearate, vinyl 2-ethylhexanoate, vinyl dodecanoate, vinyl tetradecanoate, vinyl hexadecanoate and the like including mixtures of said monomers, all of which are suitable for incorporation of the aliphatic hydrocarbon moiety.

Also suitable for incorporation of the aliphatic hydrocarbon moiety, but less preferred, are the α -unsaturated and β -unsaturated olefinic hydrocarbon derivatives such as 1-octadecene, 1-dodecene, 1-hexadecene, 1-heptadecene, 1-tridecene, 1-undecene, 1-decene, 1-pentadecene, 1-tetradecene, 2-octadecene, 2-dodecene, 2-hexadecene, 2-heptadecene, 2-tridecene, 2-undecene, 2-decene, 2-pentadecene, 2-tetradecene, and the like including mixtures of said monomers. They can be incorporated into any vinyl type polymer such as polyacrylamide, polyvinyl alcohol, polyacrylic acid, polyvinyl acetate, polymethacrylic acid, polyitaconic, poly(maleic acid), poly(maleic anhydride), polyacrylonitrile and the like. For the purposes of papermaking, the polyacrylamides,

polyvinyl alcohols and polyacrylic acids are most preferred. They would be incorporated directly into the polymer via copolymerization with the associated ethylenically unsaturated monomers including acrylamide, vinyl alcohol, acrylic acid, methacrylic acid, itaconic acid, maleic acid, acrylonitrile and the like including mixtures of said monomers during the polymerization process as described below. The description shown is specific for a polyacrylamide but is applicable to any vinyl type polymer. When incorporated in such a manner the long chain aliphatic groups are arranged on the polymer in a pendant fashion.

Suitable monomers for incorporating a charge functionality into the polymer include, but are not limited to methacryloyloxyethyl trimethyl ammonium methosulfate (METAMS); dimethyldiallyl ammonium chloride (DMDAAC); 3-acryloamido-3-methyl butyl trimethyl ammonium chloride (AMBTAC); trimethylamino methacrylate; vinyl benzyl trimethyl ammonium chloride (VBTAC), 3-allyloxy-2-hydroxy-1propane sulfonic acid sodium salt and the like including mixtures of said monomers.

Suitable monomers for incorporating a functionality for making the polymer into a form suitable for papermaking includes but is not limited to: ethylene glycol acrylate, ethylene glycol methacrylate, diethylene glycol acrylate, diethylene glycol methacrylate, 2-allyloxyethanol, 3-allyloxy-1,2-propanediol, poly(ethylene glycol) acrylate, poly(ethylene glycol) methacrylate, poly(ethylene glycol) diacrylate, poly(ethylene glycol) dimethacrylate, poly(ethylene glycol) methyl ether acrylate, poly(ethylene glycol) methyl ether methacrylate, poly(ethylene glycol) ethyl ether acrylate, poly(ethylene glycol) ethyl ether methacrylate, poly(ethylene glycol) divinyl ether, poly(ethylene glycol) phenyl ether acrylate, poly(propylene glycol) acrylate, poly(propylene glycol) methacrylate, poly(propylene glycol) diacrylate, poly(propylene glycol) dimethacrylate, poly(propylene glycol) methyl ether acrylate, poly(propylene glycol) methyl ether methacrylate, poly(propylene glycol) ethyl ether acrylate, poly(propylene glycol) ethyl ether methacrylate, poly(propylene glycol) phenyl ether acrylate and the like including mixtures of said monomers.

Note that where acrylamide is employed that the resultant polymers contain pendant amide functionality that is capable of being glyoxylated to form materials possessing temporary wet strength as shown in Figures 7 and 8.

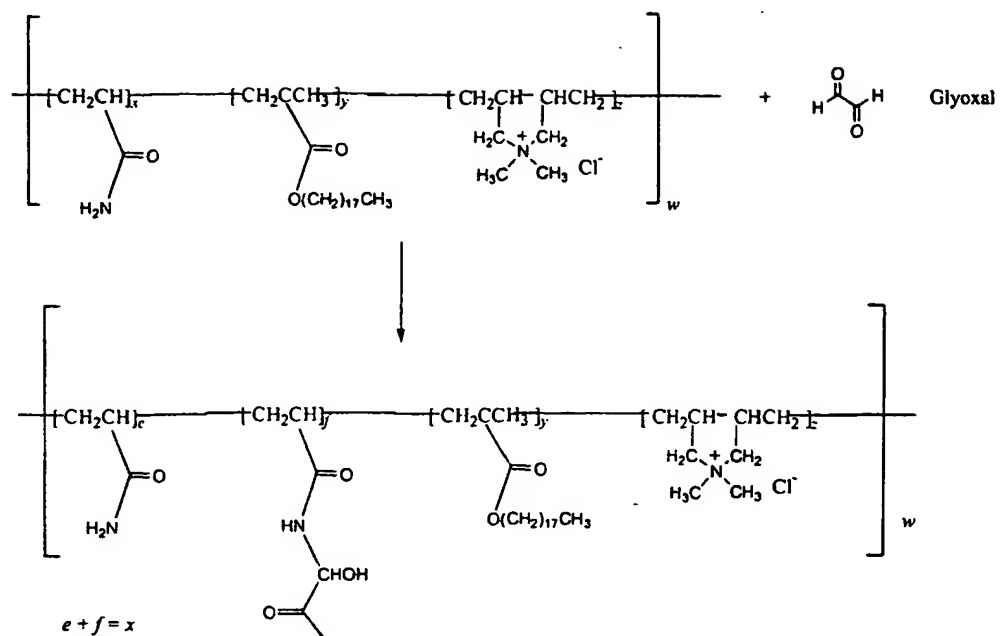


Figure 7

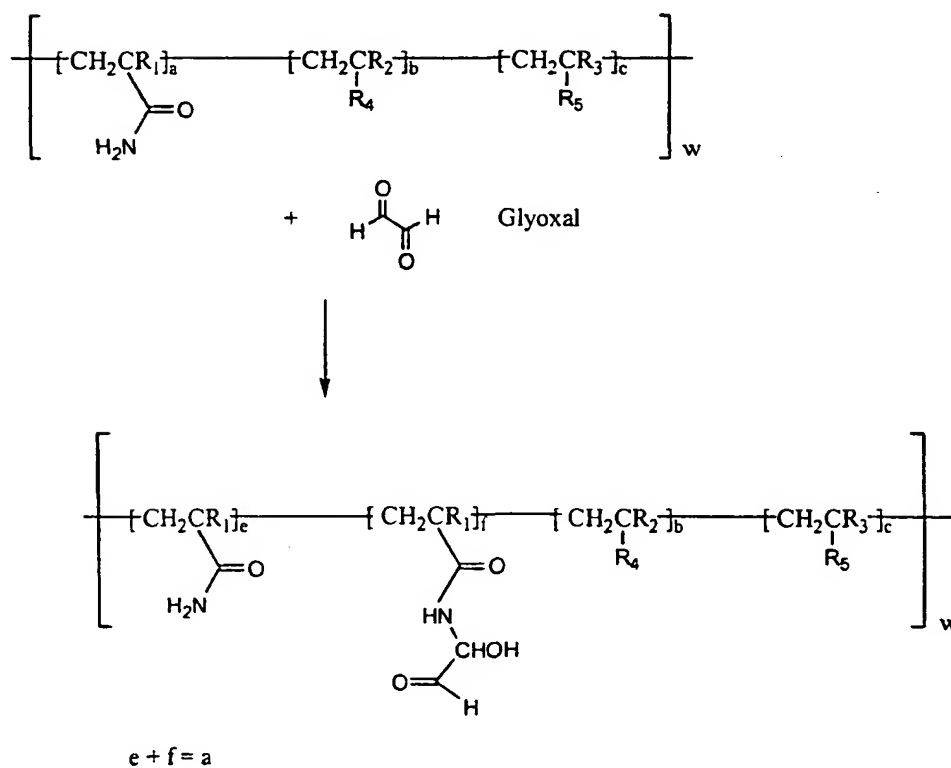


Figure 8

Where:

$w \geq 1$;

$R_1, R_1', R_2, R_3 = H, C_{1-4} \text{ alkyl}$;

$a, b > 0$;

5 $c, d \geq 0$;

$R_4 = Z - R_6 - Y$ radical where:

$Z = \text{Aryl, CH}_2, \text{COO}^-, \text{CONR}'^-, -\text{O}-, -\text{S}-, -\text{OSO}_2\text{O}-, -\text{CONHCO}-, -\text{CONHCHOHCHOO}-,$
any radical capable of bridging the R_6 group to the vinyl backbone portion of the molecule. ($R' = H, \text{alkyl}$);

10 $R_6 =$ any aliphatic, linear or branched, saturated or unsaturated, substituted or non-substituted hydrocarbon;

$Y = H, -N+R_7R_8R_9, -NR_7R_8$, where R_7, R_8, R_9 are same or different and are H or C_{1-30} linear or branched, saturated or unsaturated aliphatic hydrocarbons;

At least one of R_6, R_7, R_8, R_9 must be an aliphatic, linear or branched, substituted or non-substituted, hydrocarbon of chain length 8 or higher;

15

$R_5 = Z_2 - R_{10} - X$;

$Z_2 = \text{Aryl, CH}_2, \text{COO}^-, \text{CONH}-, -\text{O}-, -\text{S}-, -\text{OSO}_2\text{O}-$, any radical capable of bridging the R_{10} group to the vinyl backbone portion of the molecule;

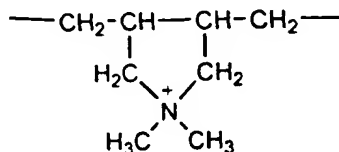
$R_{10} =$ any linear or branched, aliphatic or aromatic hydrocarbon of 2 or more carbons,

20 preferably $-(\text{CH}_2\text{CH}_2)-, -\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_2-$; and

$X = -N+R_{11}, R_{12}, R_{13}$ where R_{11}, R_{12}, R_{13} is a C_{1-4} alkyl group.

R_5 may also be the residue formed by co-polymerization with dimethyldiallyl ammonium chloride. In this case the residue will be the form of monomers with repeat units of structure:

25

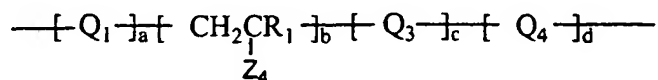


Derivatization of functional groups on the polymer backbone:

The third approach to synthesis of materials of this invention is to modify the functional groups on the polymer backbone. The vinyl type polymers such as polyacrylamides, modified polyacrylamides, polyacrylic acids, polyvinyl alcohols, polymaleic acid, polymaleic anhydride and polyacrylonitriles contain functional groups

which may be further derivatized to produce materials of the structure of Figure 4. The polymer functional groups which may be reacted upon include but are not limited to: amide, carboxyl, hydroxyl, anhydride, cyano, thiol and aldehyde (from glyoxylation or similar reaction). In general the starting polymer will be one of that shown in Figure 9.

5

**Figure 9**

where:

10 $\text{R}_1 = \text{H}, \text{C}_{1-4} \text{ alkyl};$

$a, b \geq 1;$

$c, d \geq 0;$

$\text{Q}_1 =$ a monomer unit or a block or graft copolymer containing a pendant group capable of forming hydrogen or covalent bonds with cellulose. Preferred pendant groups for hydrogen bonding are ---CONH_2 , $\text{---COO}^- \text{M}^+$, ---OH and mixtures of said groups. Preferred pendant groups for covalent bonding are aldehydes and anhydrides. M^+ can be any suitable counter ion including Na^+ , K^+ , Ca^{+2} and the like;

$\text{Q}_3 =$ a monomer unit or a block or graft copolymer containing a charge functionality. Such charge functionality is preferably cationic but may be anionic or amphoteric;

20 $\text{Z}_4 =$ ---CONHCHOHCHO , ---CHO , ---CONH_2 , ---COOH , ---CN , ---OH , ---SH , ---NH_2 , ---R'OH , ---R'CHO , ---R'CONH_2 , ---R'COOH , ---R'CN , ---R'OH , ---R'SH , ---R'NH_2 or any other functional group capable of being reacted upon in a manner so as to incorporate a C_8 or higher linear or branched, saturated or unsaturated, substituted or unsubstituted aliphatic hydrocarbon into the polymer and R' can be any bridging radical, organic or inorganic whose purpose is to attach the functional group to the polymer; and

$\text{Q}_4 =$ a monomer unit or a block or graft copolymer containing a hydrophilic moiety, which is desirable for making the material into a form suitable for papermaking. Q_4 may take the form of $\text{---Z}_2\text{---Q}_4\text{---Z}_2\text{'}$ where Z_2 , $\text{Z}_2\text{'}$ are any bridging radicals, the same or different, whose purpose is to provide incorporation into the polymer backbone and Q_4 is as defined previously. Q_4 may be incorporated to offset the increased polymer hydrophobicity caused by introduction of the aliphatic hydrocarbon moieties. Examples of suitable Q_4 moieties are (but is not limited to) the aliphatic polyether derivatives of the formula $\text{---}[(\text{CR}_1\text{R}_2)_x\text{O}]_y\text{---R}_3$, wherein R_1 , R_2 is H or

30

CH_3 , $x \geq 2$, $y \geq 2$ and R_3 is any suitable terminal group including $-\text{CH}_3$, $-\text{H}$, $-\text{C}_2\text{H}_5$, $-\text{NH}_2$.

Such structures as those shown in Figure 9 are amenable to reaction with a large variety of reagents as a means of incorporating aliphatic residues into the polymer. The general scheme for such syntheses is shown in Figure 10.

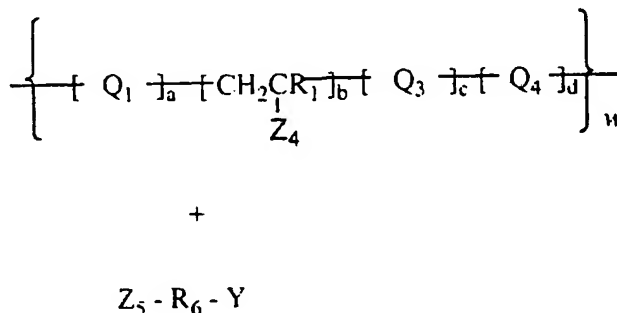


Figure 10

10 where:

$\text{R}_1 = \text{H}$, C_{1-4} alkyl;

$a, b \geq 1$;

$c, d \geq 0$;

15 $\text{Q}_1 =$ a monomer unit or a block or graft copolymer containing a pendant group capable of forming hydrogen or covalent bonds with cellulose. Preferred pendant groups for hydrogen bonding are $-\text{CONH}_2$, $-\text{COO}^- \text{M}^+$, $-\text{OH}$ and mixtures of said groups. Preferred pendant groups for covalent bonding are aldehydes and anhydrides. M^+ can be any suitable counter ion including Na^+ , K^+ , Ca^{+2} and the like;

$\text{Q}_3 =$ a monomer unit or a block or graft copolymer containing a charge functionality.

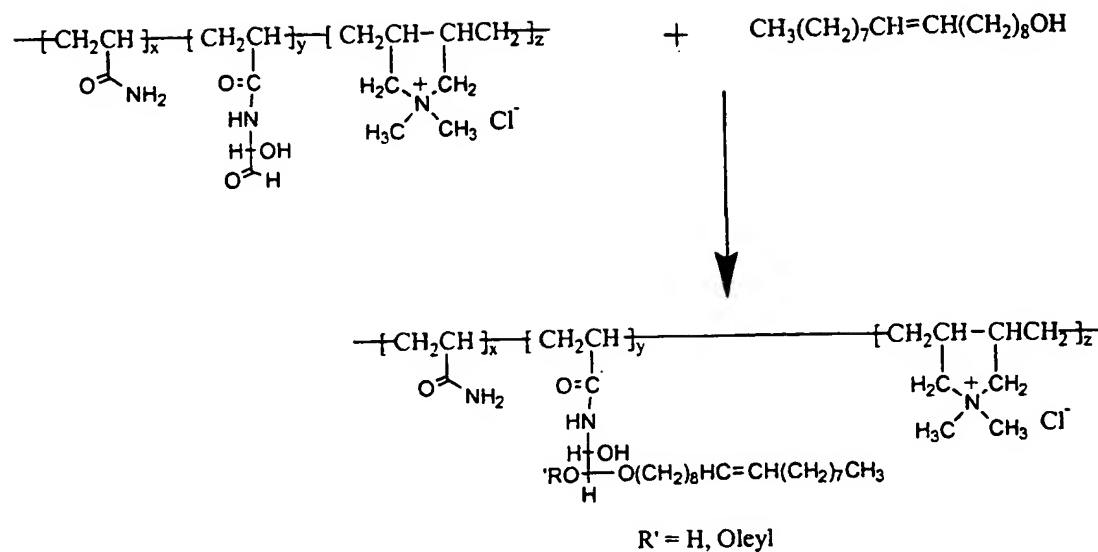
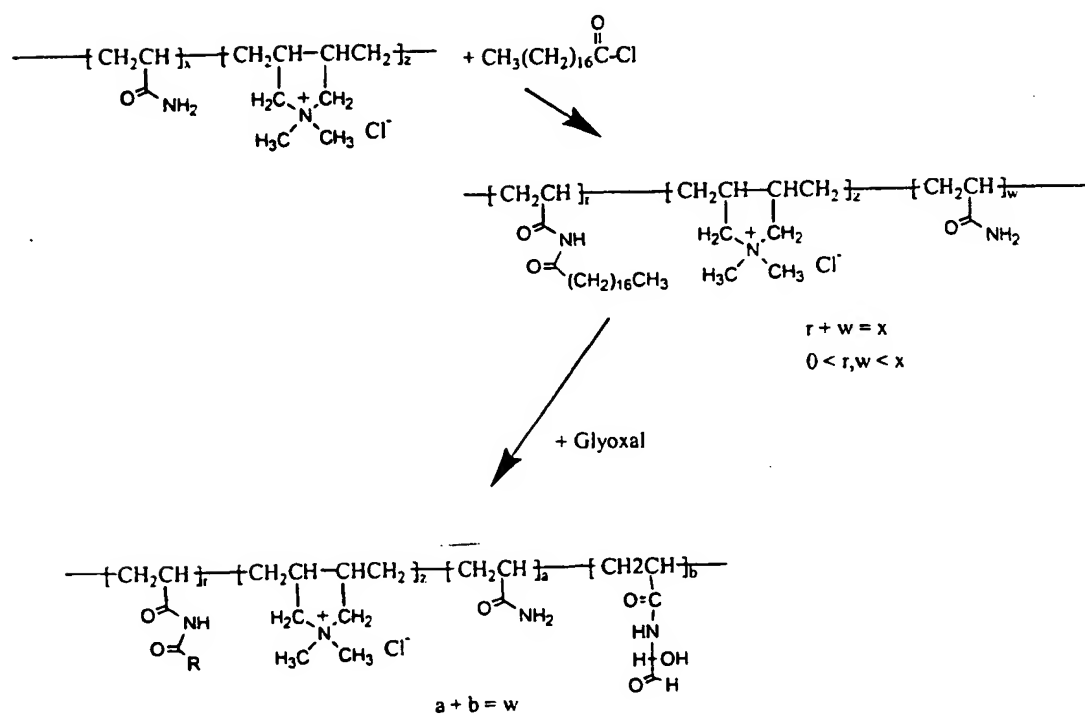
20 Such charge functionality is preferably cationic but may be anionic or amphoteric;

$\text{Z}_4 = -\text{CONHCHOHCHO}$, $-\text{CHO}$, $-\text{CONH}_2$, $-\text{COOH}$, $-\text{CN}$, $-\text{OH}$, $-\text{SH}$, $-\text{NH}_2$, $-\text{R}'\text{OH}$,

$-\text{R}'\text{CHO}$, $-\text{R}'\text{CONH}_2$, $-\text{R}'\text{COOH}$, $-\text{R}'\text{CN}$, $-\text{R}'\text{OH}$, $-\text{R}'\text{SH}$, $-\text{R}'\text{NH}_2$ or any other

25 functional group capable of being reacted upon in a manner so as to incorporate a C_8 or higher linear or branched, saturated or unsaturated, substituted or unsubstituted aliphatic hydrocarbon into the polymer and R' can be any bridging radical, organic or inorganic whose purpose is to attach the functional group to the polymer; and

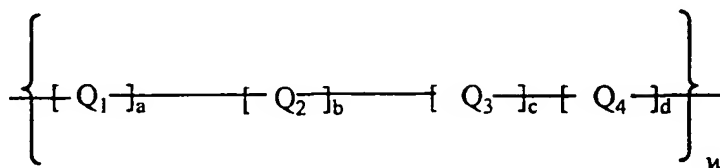
- Q_4 = a monomer unit or a block or graft copolymer containing a hydrophilic moiety, which is desirable for making the material into a form suitable for papermaking. Q_4 may take the form of $-Z_2-Q_4-Z_2'$ where Z_2, Z_2' are any bridging radicals, the same or different, whose purpose is to provide incorporation into the polymer backbone and Q_4 is as defined previously. Q_4 may be incorporated to offset the increased polymer hydrophobicity caused by introduction of the aliphatic hydrocarbon moieties. Examples of suitable Q_4 moieties are (but is not limited to) the aliphatic polyether derivatives of the formula $-(CR_1R_2)_xO)_y-R_3$, wherein R_1, R_2 is H or CH_3 , $x \geq 2$, $y \geq 2$ and R_3 is any suitable terminal group including $-CH_3, -H, -C_2H_5, -NH_2$.
- Z_5 = $HOOC-, ClOC-, HO-, HS-, -COOOC-, H_2N-, HCO-, ClSO_2O-, XOC-$ (X = halo), $ClCOO-$, or any other functional group capable of reaction with a Z_4 type functional group so as to attach the $-R_6-Y$ residue onto the polymer;
- R_6 = any aliphatic, linear or branched, saturated or unsaturated, substituted or non-substituted hydrocarbon;
- Y = $H, -N^+R_7R_8R_9, -NR_7R_8$, where R_7, R_8, R_9 are same or different and are H or C_{1-30} linear or branched, saturated or unsaturated aliphatic hydrocarbons; and where at least one of R_6, R_7, R_8, R_9 must be a C_8 or higher linear or branched, substituted or non-substituted, aliphatic hydrocarbon.
- Some specific examples of such reactions are given in Figures 11 and 12.

**Figure 11****Figure 12**

- 5 It will be appreciated that the foregoing examples, given for purposes of illustration, are not to be construed as limiting the scope of this invention, which is defined by the following claims and all equivalents thereto.

We claim:

1. A synthetic polymer containing one or more aliphatic hydrocarbon moieties, said synthetic polymer having the following structure:



where:

$a, b > 0$;

$c, d \geq 0$ such that $c+d > 0$;

$w \geq 1$;

Q_1 = a monomer unit or a block or graft copolymer containing a pendant group capable of forming hydrogen or covalent bonds with cellulose;

Q_2 = a monomer unit or a block or graft copolymer containing a C_8 or higher linear or branched, saturated or unsaturated, substituted or unsubstituted aliphatic hydrocarbon moiety;

Q_3 = a monomer unit or a block or graft copolymer containing a charge functionality; and

Q_4 = a monomer unit or a block or graft copolymer containing a hydrophilic moiety, which is desirable for making the material into a form suitable for papermaking.

2. The polymer of claim 1 wherein the pendant group on Q_1 capable of forming hydrogen or covalent bonds is selected from the group consisting of $-\text{CONH}_2$, $-\text{COOH}$, $-\text{COO}^-\text{M}^+$, $-\text{OH}$, $-\text{CONHCHOHCHO}$ and mixtures thereof, wherein M^+ is a counter ion.

3. The polymer of claim 1 wherein Q_2 is of the form $-\text{Z}_1-\text{Q}_2-\text{Z}_1'-$ where Z_1, Z_1' are bridging radicals, which can be the same or different.

4. The polymer of claim 1 wherein Q_4 is of the form $-\text{Z}_2-\text{Q}_4-\text{Z}_2'-$ where Z_2, Z_2' are bridging radicals, which can be the same or different.

5. The polymer of claim 1 wherein Q_4 is a radical of the form $—CHR_1CR_0R_1'—$ wherein R_0 is an aliphatic polyether derivative of the formula $—[(CR_2R_2')_xO]_y—R_3$

where:

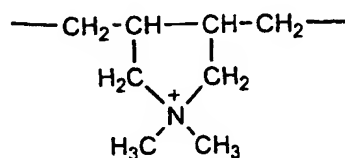
R_1, R_1' is -H, C_{1-4} alkyl;

R_2, R_2' is -H or $-CH_3$;

$x \geq 2$;

$y \geq 2$; and

R_3 is a terminal group selected from the group consisting of $-CH_3$, -H, $-C_2H_5$, and NH_2 .



6. The polymer of claim 1 wherein Q_3 is

7. The polymer of claim 1 wherein Q_3 is a radical of the form $—CHR_1CR_0R_1'—$ wherein R_0 = a pendant group of the form $Z_1-R_{10}-W$, where Z_1 is a radical bonding the R_{10} group to the polymer;

R_1 and R_1' are -H or a C_{1-4} alkyl group;

R_{10} = any linear or branched, aliphatic or aromatic hydrocarbon of 2 or more carbons; and

$W = -N+R_{11}, R_{12}, R_{13}$ where R_{11}, R_{12}, R_{13} is a C_{1-4} alkyl group.

8. The polymer of claim 7 wherein Z_1 is selected from the group consisting of aryl, $-CH_2-$, $-COO-$, $-CONH-$, -O-, -S-, and $-OSO_2O-$.

9. The polymer of claim 7 wherein R_{10} is $-(CH_2CH_2)-$ or $-C(CH_3)_2CH_2CH_2-$.

10. The polymer of claim 1 wherein "c" is 0.

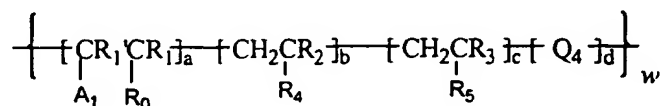
11. The polymer of claim 1 wherein "d" is 0.

12. The polymer of claim 1 wherein the pendant group on Q_1 capable of forming hydrogen bonds is $-CONH_2$.

13. The polymer of claim 1 wherein the pendant group on Q_1 capable of forming covalent bonds is $-CONHCHOHCHO$.

14. The polymer of claim 1 wherein Q_1 has $-\text{CONH}_2$ and $-\text{CONHCHOHCHO}$ pendant groups.

15. A synthetic polymer having hydrogen bonding capability and containing one or more aliphatic hydrocarbon moieties, said polymer having the following structure:



where:

$w \geq 1$;

$R_1, R_1', R_2, R_3 = \text{H or } C_{1-4} \text{ alkyl}$;

$a, b > 0$;

$c, d \geq 0$ such that $c+d > 0$;

$R_0 =$ a group capable of forming hydrogen or covalent bonds with cellulose;

$Q_4 =$ a monomer unit or a block or graft copolymer containing a hydrophilic moiety;

$A_1 = -\text{H}, -\text{COOH}$;

$R_4 =$ a $Z_1 - R_6 - Y$ radical,

where:

$Z_1 =$ any radical capable of bonding the R_6 group to the polymer;

$R_6 =$ any linear or branched, saturated or unsaturated, substituted or non-substituted aliphatic hydrocarbon;

$Y = -\text{H}, -\text{N}^+R_7R_8R_9$, or $-\text{NR}_7R_8$, where R_7, R_8, R_9 are same or different and are H or C_{1-30} linear or branched, saturated or unsaturated aliphatic hydrocarbons and where:

at least one of R_6, R_7, R_8, R_9 must be a linear or branched, substituted or non-substituted, aliphatic hydrocarbon having a carbon chain length of 8 or higher;

$R_5 = Z_1 - R_{10} - W$,

where:

$Z_1 =$ any radical capable of bonding the R_{10} group to the polymer;

$R_{10} =$ any linear or branched, aliphatic or aromatic hydrocarbon of 2 or more carbons; and

$W = -\text{N}^+R_{11}R_{12}R_{13}$, where R_{11}, R_{12}, R_{13} are C_{1-4} alkyl groups.

16. The polymer of claim 15 wherein R_0 is selected from the group consisting of $-\text{CONH}_2$, $-\text{COOH}$, $-\text{COO}^+\text{M}^+$, $-\text{OH}$, $-\text{CONHCHOHCHO}$, and mixtures thereof, wherein M^+ is a counter ion.

17. The polymer of claim 15 wherein Q_4 is of the form $-\text{Z}_2-\text{Q}_4-\text{Z}_2'$ where Z_2 , Z_2' are bridging radicals, which can be the same or different.

18. The polymer of claim 15 wherein Z_1 is selected from the group consisting of aryl, $-\text{CH}_2-$, $-\text{COO}-$, $-\text{CONR}'-$, $-\text{O}-$, $-\text{S}-$, $-\text{OSO}_2\text{O}-$, $-\text{CONHCO}-$, and $-\text{CONHCHOHCHOO}-$, and where R' is H or C_{1-4} alkyl.

19. The polymer of claim 15 wherein R_5 is $\text{Z}_1-\text{R}_{10}-\text{W}$.

20. The polymer of claim 19 wherein Z_1 is selected from the group consisting of aryl, $-\text{CH}_2-$, $-\text{COO}-$, $-\text{CONH}-$, $-\text{O}-$, $-\text{S}-$, and $-\text{OSO}_2\text{O}-$.

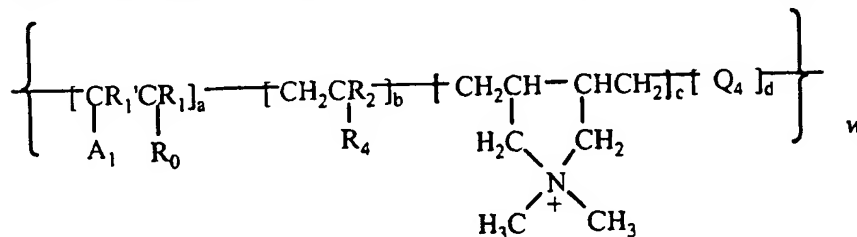
21. The polymer of claim 19 wherein R_{10} is $-(\text{CH}_2\text{CH}_2)-$ or $-\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_2-$.

22. The polymer of claim 15 wherein A_1 is $-\text{H}$ and R_0 is $-\text{CONH}_2$.

23. The polymer of claim 15 wherein A_1 is $-\text{H}$ and R_0 is $-\text{CONHCHOHCHO}$.

24. The polymer of claim 15 wherein R_0 consists of both $-\text{CONH}_2$ and $-\text{CONHCHOHCHO}$ groups.

25. A synthetic polymer having hydrogen bonding capability and containing one or more aliphatic hydrocarbon moieties, said polymer having the following structure:



where:

$$w \geq 1;$$

$$R_1, R_1', R_2, R_3 = \text{H or } C_{1-4} \text{ alkyl};$$

$$a, b > 0;$$

$$c, d \geq 0 \text{ such that } c+d > 0;$$

R_0 = a group capable of forming hydrogen or covalent bonds with cellulose;

Q_4 = a monomer unit or a block or graft copolymer containing a hydrophilic moiety;

$$A_1 = -\text{H}, -\text{COOH};$$

$$R_4 = \text{a } Z_1 - R_6 - Y \text{ radical,}$$

where:

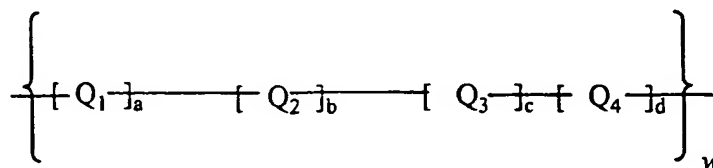
Z_1 = any radical capable of bonding the R_6 group to the polymer;

R_6 = any linear or branched, saturated or unsaturated, substituted or non-substituted aliphatic hydrocarbon;

Y = $-\text{H}$, $-\text{N}^+R_7R_8R_9$, or $-\text{NR}_7R_8$, where R_7, R_8, R_9 are same or different and are H or C_{1-30} linear or branched, saturated or unsaturated aliphatic hydrocarbons and where:

at least one of R_6, R_7, R_8, R_9 must be a linear or branched, substituted or non-substituted, aliphatic hydrocarbon having a carbon chain length of 8 or higher.

26. A paper sheet comprising a synthetic polymer having hydrogen bonding capability and containing one or more aliphatic hydrocarbon moieties, said polymer having the following structure:



where:

$$a, b > 0;$$

$$c, d \geq 0;$$

$$w \geq 1;$$

Q_1 = a monomer unit or a block or graft copolymer containing a pendant group capable of forming hydrogen or covalent bonds with cellulose;

Q_2 = a monomer unit or a block or graft copolymer containing a C_8 or higher linear or branched, saturated or unsaturated, substituted or unsubstituted aliphatic hydrocarbon moiety;

Q_3 = a monomer unit or a block or graft copolymer containing a charge functionality; and

Q_4 = a monomer unit or a block or graft copolymer containing a hydrophilic moiety, which is desirable for making the material into a form suitable for papermaking.

27. The paper sheet of claim 26 wherein the pendant group on Q_1 capable of forming hydrogen or covalent bonds is selected from the group consisting of $-CONH_2$, $-COOH$, $-COO^+M^+$, $-OH$, $-CONHCHOHCHO$ and mixtures thereof, wherein M^+ is a counter ion.

28. The paper sheet of claim 26 wherein Q_2 is of the form $-Z_1-Q_2-Z_1'$ where Z_1, Z_1' are bridging radicals, which can be the same or different.

29. The paper sheet of claim 26 wherein Q_4 is of the form $-Z_2-Q_4-Z_2'$ where Z_2, Z_2' are bridging radicals, which can be the same or different.

30. The paper sheet of claim 26 wherein Q_4 is a radical of the form $-CHR_1CR_0R_1'$ wherein R_0 is an aliphatic polyether derivative of the formula $-(CR_2R_2')_xO)_y-R_3$ where:

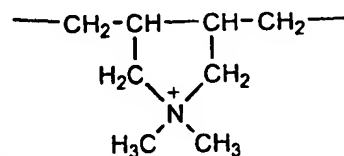
R_1, R_1' is $-H, C_{1-4}$ alkyl;

R_2, R_2' is $-H$ or $-CH_3$;

$x \geq 2$;

$y \geq 2$; and

R_3 is a terminal group selected from the group consisting of $-CH_3$, $-H$, $-C_2H_5$, and $-NH_2$.



31. The paper sheet of claim 26 wherein Q_3 is

32. The paper sheet of claim 26 wherein Q_3 is a radical of the form $\text{---CHR}_1CR_0R_1'\text{---}$ wherein

R_0 = a pendant group of the form $Z_1-R_{10}-W$ where Z_1 is a radical capable of bonding the R_{10} group to the polymer;

R_1 and R_1' are -H or a C_{1-4} alkyl group;

R_{10} = any linear or branched, aliphatic or aromatic hydrocarbon of 2 or more carbons; and

$W = -N+R_{11}, R_{12}, R_{13}$ where R_{11}, R_{12}, R_{13} is a C_{1-4} alkyl group.

33. The paper sheet of claim 32 wherein Z_1 is selected from the group consisting of aryl, $-CH_2-$, $-COO-$, $-CONH-$, $-O-$, $-S-$, and $-OSO_2O-$.

34. The paper sheet of claim 32 wherein R_{10} is $-(CH_2CH_2)-$ or $-C(CH_3)_2CH_2CH_2-$.

35. The paper sheet of claim 26 wherein "c" is 0.

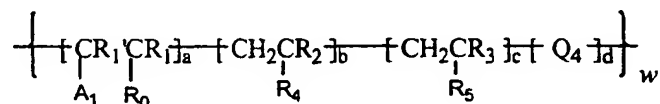
36. The paper sheet of claim 26 wherein "d" is 0.

37. The paper sheet of claim 26 wherein the pendant group on Q_1 capable of forming hydrogen bonds is $-CONH_2$.

38. The paper sheet of claim 26 wherein the pendant group on Q_1 capable of forming covalent bonds is $-CONHCHOHCHO$.

39. The paper sheet of claim 26 wherein Q_1 has $-CONH_2$ and $-CONHCHOHCHO$ pendant groups.

40. A paper sheet comprising a synthetic polymer having hydrogen bonding capability and containing one or more aliphatic hydrocarbon moieties, said polymer having the following structure:



where:

$w \geq 1$;

$R_1, R_1', R_2, R_3 = H$ or C_{1-4} alkyl;

$a, b > 0$;

$c, d \geq 0$;

$R_0 =$ a group capable of forming hydrogen or covalent bonds with cellulose;

Q_4 = a monomer unit or a block or graft copolymer containing a hydrophilic moiety;

A_1 = -H, -COOH;

R_4 = a Z_1 - R_6 - Y radical,

where:

Z_1 = any radical capable of bonding the R_6 group to the polymer;

R_6 = any linear or branched, saturated or unsaturated, substituted or non-substituted aliphatic hydrocarbon;

Y = -H, -N^{*} $R_7R_8R_9$, or -NR₇R₈, where R_7 , R_8 , R_9 are same or different and are H or C₁₋₃₀ linear or branched, saturated or unsaturated aliphatic hydrocarbons and where:

at least one of R_6 , R_7 , R_8 , R_9 must be a linear or branched, substituted or non-substituted, aliphatic hydrocarbon having a carbon chain length of 8 or higher;

R_5 = Z_1 - R_{10} -W,

where:

Z_1 = any radical capable of bonding the R_{10} group to the polymer;

R_{10} = any linear or branched, aliphatic or aromatic hydrocarbon of 2 or more carbons; and

W = -N^{*} $R_{11}R_{12}R_{13}$, where R_{11} , R_{12} , R_{13} are C₁₋₄ alkyl groups.

41. The paper sheet of claim 40 wherein R_6 is selected from the group consisting of -CONH₂, -COOH, -COO⁻M⁺, -OH, -CONHCHOHCHO, and mixtures thereof, wherein M⁺ is a counter ion.

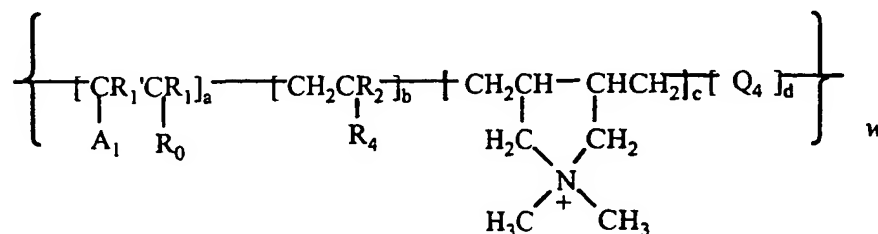
42. The paper sheet of claim 40 wherein Q_4 is of the form - Z_2 - Q_4 - Z_2' - where Z_2 , Z_2' are bridging radicals, which can be the same or different.

43. The paper sheet of claim 40 wherein Z_1 is selected from the group consisting of aryl, -CH₂-, -COO-, -CONR'-, -O-, -S-, -OSO₂O-, -CONHCO-, and -CONHCHOHCHOO-, and where R' is H or C₁₋₄ alkyl.

44. The paper sheet of claim 40 wherein R_5 is Z_1 - R_{10} -W.

45. The paper sheet of claim 44 wherein Z_1 is selected from the group consisting of aryl, -CH₂-, -COO-, -CONH-, -O-, -S-, and -OSO₂O-.

46. The paper sheet of claim 44 wherein R_{10} is $-(CH_2CH_2)-$ or $-C(CH_3)_2CH_2CH_2-$.
47. The paper sheet of claim 40 wherein A_1 is $-H$ and R_0 is $-CONH_2$.
48. The paper sheet of claim 40 wherein A_1 is $-H$ and R_0 is $-CONHCHOHCHO$.
49. The paper sheet of claim 40 wherein R_0 consists of both $-CONH_2$ and $-CONHCHOHCHO$ groups.
50. A paper sheet comprising a synthetic polymer having hydrogen bonding capability and containing one or more aliphatic hydrocarbon moieties, said polymer having the following structure:



where:

 $w \geq 1;$

$R_1, R_1', R_2, R_3 = \text{H or } C_{1-4} \text{ alkyl;}$

a, b > 0;

$c, d \geq 0$ such that $c + d > 0$;

R_0 = a group capable of forming hydrogen or covalent bonds with cellulose;

Q₄ = a monomer unit or a block or graft copolymer containing a hydrophilic moiety;

$$A_1 = -H, -COOH;$$
$$R_4 = \text{a } Z_1 - R_6 - Y \text{ radical,}$$

where:

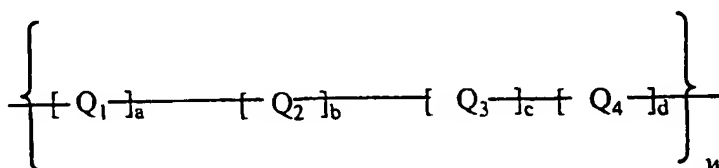
$Z_1 =$ any radical capable of bonding the R_6 group to the polymer;

R₆ = any linear or branched, saturated or unsaturated, substituted or non-substituted aliphatic hydrocarbon;

Y = -H, -N⁺R₇R₈R₉, or -NR₇R₈, where R₇, R₈, R₉ are same or different and are H or C₁₋₃₀ linear or branched, saturated or unsaturated aliphatic hydrocarbons and where:

at least one of R_6 , R_7 , R_8 , R_9 must be a linear or branched, substituted or non-substituted, aliphatic hydrocarbon having a carbon chain length of 8 or higher.

51. A method of making a paper sheet comprising the steps of: (a) forming an aqueous suspension of papermaking fibers; (b) depositing the aqueous suspension of papermaking fibers onto a forming fabric to form a web; and (c) dewatering and drying the web to form a paper sheet, wherein a synthetic polymer is added to the aqueous suspension of fibers and/or the web, said polymer having the following structure:



where:

$a, b > 0$;

$c, d \geq 0$;

$w \geq 1$;

Q_1 = a monomer unit or a block or graft copolymer containing a pendant group capable of forming hydrogen or covalent bonds with cellulose;

Q_2 = a monomer unit or a block or graft copolymer containing a C_8 or higher linear or branched, saturated or unsaturated, substituted or unsubstituted aliphatic hydrocarbon moiety;

Q_3 = a monomer unit or a block or graft copolymer containing a charge functionality; and

Q_4 = a monomer unit or a block or graft copolymer containing a hydrophilic moiety, which is desirable for making the material into a form suitable for papermaking.

52. The method of claim 51 wherein the pendant group on Q_1 capable of forming hydrogen or covalent bonds is selected from the group consisting of $-\text{CONH}_2$, $-\text{COOH}$, $-\text{COO}^-\text{M}^+$, $-\text{OH}$, $-\text{CONHCHOHCHO}$ and mixtures thereof, wherein M^+ is a counter ion.

53. The method of claim 51 wherein Q_2 is of the form $-\text{Z}_1-\text{Q}_2-\text{Z}_1'$ where Z_1 , Z_1' are bridging radicals, which can be the same or different.

54. The method of claim 51 wherein Q_4 is of the form $-\text{Z}_2-\text{Q}_4-\text{Z}_2'$ where Z_2 , Z_2' are bridging radicals, which can be the same or different.

55. The method of claim 51 wherein Q_4 is a radical of the form $—CHR_1CR_0R_1'—$ wherein R_0 is an aliphatic polyether derivative of the formula $—[(CR_2R_2')_xO]_y—R_3$

where:

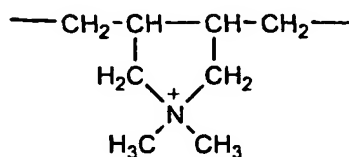
R_1, R_1' is -H, C_{1-4} alkyl;

R_2, R_2' is -H or $-CH_3$;

$x \geq 2$;

$y \geq 2$; and

R_3 is a terminal group selected from the group consisting of $-CH_3$, -H, $-C_2H_5$, and $-NH_2$.



56. The method of claim 51 wherein Q_3 is

57. The method of claim 51 wherein Q_3 is a radical of the form $—CHR_1CR_0R_1'—$ wherein R_0 = a pendant group of the form $Z_1-R_{10}-W$, where Z_1 is a radical capable of bonding the R_{10} group to the polymer;

R_1 and R_1' are -H or a C_{1-4} alkyl group;

R_{10} = any linear or branched, aliphatic or aromatic hydrocarbon of 2 or more carbons; and

$W = -N+R_{11}, R_{12}, R_{13}$ where R_{11}, R_{12}, R_{13} is a C_{1-4} alkyl group.

58. The method of claim 57 wherein Z_1 is selected from the group consisting of aryl, $-CH_2-$,

$-COO-$, $-CONH-$, $-O-$, $-S-$, and $-OSO_2O-$.

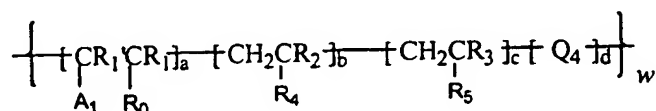
59. The method of claim 57 wherein R_{10} is $-(CH_2CH_2)-$ or $-C(CH_3)_2CH_2CH_2-$.

60. The method of claim 51 wherein "c" is 0.

61. The method of claim 51 wherein "d" is 0.

62. The method of claim 51 wherein the pendant group on Q_1 capable of forming hydrogen bonds is $-CONH_2$.

63. The method of claim 51 wherein the pendant group on Q_1 capable of forming covalent bonds is $-\text{CONHCHOHCHO}$.
64. The method of claim 51 wherein Q_1 has $-\text{CONH}_2$ and $-\text{CONHCHOHCHO}$ pendant groups.
65. A method of making a paper sheet comprising the steps of: (a) forming an aqueous suspension of papermaking fibers; (b) depositing the aqueous suspension of papermaking fibers onto a forming fabric to form a web; and (c) dewatering and drying the web to form a paper sheet, wherein a synthetic polymer is added to the aqueous suspension of fibers and/or the web, said polymer having the following structure:



where:

$w \geq 1$;

$R_1, R_1', R_2, R_3 = \text{H or } C_{1-4} \text{ alkyl}$;

$a, b > 0$;

$c, d \geq 0$;

$R_0 =$ a group capable of forming hydrogen or covalent bonds with cellulose;

$Q_4 =$ a monomer unit or a block or graft copolymer containing a hydrophilic moiety;

$A_1 = -\text{H}, -\text{COOH}$;

$R_4 =$ a $Z_1 - R_6 - Y$ radical,

where:

$Z_1 =$ any radical capable of bonding the R_6 group to the polymer;

$R_6 =$ any linear or branched, saturated or unsaturated, substituted or non-substituted aliphatic hydrocarbon;

$Y = -\text{H}, -\text{N}^*R_7R_8R_9$, or $-\text{NR}_7R_8$, where R_7, R_8, R_9 are same or different and are H or C_{1-30} linear or branched, saturated or unsaturated aliphatic hydrocarbons and where:

at least one of R_6, R_7, R_8, R_9 must be a linear or branched, substituted or non-substituted, aliphatic hydrocarbon having a carbon chain length of 8 or higher;

$R_5 = Z_1 - R_{10} - W$,

where:

- Z_1 = any radical capable of bonding the R_{10} group to the polymer;
 R_{10} = any linear or branched, aliphatic or aromatic hydrocarbon of 2 or more carbons; and
 W = $-N^+R_{11}, R_{12}, R_{13}$, where R_{11}, R_{12}, R_{13} are C_{1-4} alkyl groups.

66. The method of claim 65 wherein R_0 is selected from the group consisting of $-\text{CONH}_2$, $-\text{COOH}$, $-\text{COO}^+\text{M}^+$, $-\text{OH}$, $-\text{CONHCHOHCHO}$, and mixtures thereof, wherein M^+ is a counter ion.

67. The method of claim 65 wherein Q_4 is of the form $-\text{Z}_2-\text{Q}_4-\text{Z}_2'$ where Z_2, Z_2' are bridging radicals, which can be the same or different.

68. The method of claim 65 wherein Z_1 is selected from the group consisting of aryl, $-\text{CH}_2-$, $-\text{COO}-$, $-\text{CONR}'$, $-\text{O}-$, $-\text{S}-$, $-\text{OSO}_2\text{O}-$, $-\text{CONHCO}-$, and $-\text{CONHCHOHCHOO}-$, and where R' is H or C_{1-4} alkyl.

69. The method of claim 65 wherein R_5 is $Z_1-R_{10}-W$.

70. The method of claim 69 wherein Z_1 is selected from the group consisting of aryl, $-\text{CH}_2-$, $-\text{COO}-$, $-\text{CONH}-$, $-\text{O}-$, $-\text{S}-$, and $-\text{OSO}_2\text{O}-$.

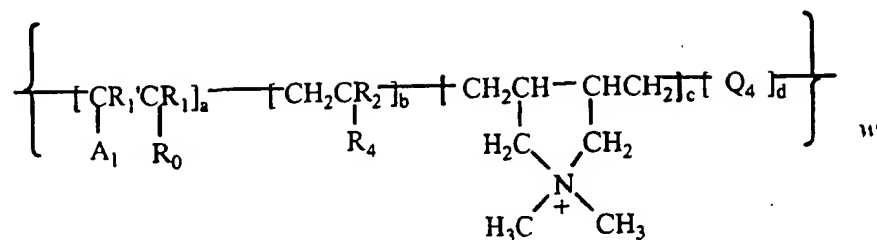
71. The method of claim 69 wherein R_{10} is $-(\text{CH}_2\text{CH}_2)-$ or $-\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_2-$.

72. The method of claim 65 wherein A_1 is $-\text{H}$ and R_0 is $-\text{CONH}_2$.

73. The method of claim 65 wherein A_1 is $-\text{H}$ and R_0 is $-\text{CONHCHOHCHO}$.

74. The method of claim 65 wherein R_0 consists of both $-\text{CONH}_2$ and $-\text{CONHCHOHCHO}$ groups.

75. . A method of making a paper sheet comprising the steps of: (a) forming an aqueous suspension of papermaking fibers; (b) depositing the aqueous suspension of papermaking fibers onto a forming fabric to form a web; and (c) dewatering and drying the web to form a paper sheet, wherein a synthetic polymer is added to the aqueous suspension of fibers and/or the web, said polymer having the following structure:



where:

 $w \geq 1;$

$R_1, R_1', R_2, R_3 = H \text{ or } C_{1-4} \text{ alkyl};$

a, b > 0;

$c, d \geq 0$ such that $c + d > 0$;

R_0 = a group capable of forming hydrogen or covalent bonds with cellulose;

Q_4 = a monomer unit or a block or graft copolymer containing a hydrophilic moiety;

$A_1 = -H, -COOH;$

$$R_4 = a Z_1 - R_6 - Y \text{ radical,}$$

where:

$Z_1 =$ any radical capable of bonding the R_6 group to the polymer;

R₆= any linear or branched, saturated or unsaturated, substituted or non-substituted aliphatic hydrocarbon;

Y = -H, -N⁺R₇R₈R₉, or -NR₇R₈, where R₇, R₈, R₉ are same or different and are H or C₁₋₃₀ linear or branched, saturated or unsaturated aliphatic hydrocarbons and where:

at least one of R₆, R₇, R₈, R₉ must be a linear or branched, substituted or non-substituted, aliphatic hydrocarbon having a carbon chain length of 8 or higher.

INTERNATIONAL SEARCH REPORT

Int'l. Application No.
PCT/US 00/01615

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F220/56 C08F220/18 C08F220/06 C08F226/04 C08F8/00
D21H17/33

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 D21H C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 372 787 A (CALGON CORP) 6 November 1974 (1974-11-06) page 1, column 1, line 34 - line 41 example 1 page 4, column 1, line 25 - column 2, line 58	1-75
X	US 5 368 744 A (WOOD MICHAEL R ET AL) 29 November 1994 (1994-11-29) examples claims	1-25
X	US 4 835 234 A (VALINT PAUL L ET AL) 30 May 1989 (1989-05-30) claims 15,16	1-25
	--- -/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

23 May 2000

Date of mailing of the international search report

06/06/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Pollio, M

INTERNATIONAL SEARCH REPORT

Int. J. Application No

PCT/US 00/01615

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 541 252 A (BRAUM MANFRED ET AL) 30 July 1996 (1996-07-30) examples	1-25
A	EP 0 374 478 A (AMERICAN CYANAMID CO) 27 June 1990 (1990-06-27) examples 11-14	1-75

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int'l Application No

PCT/US 00/01615

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 1372787 A	06-11-1974	BE 787380 A	09-02-1973
		CA 980066 A	23-12-1975
		CH 534772 A	15-03-1973
		DE 2239208 A	22-02-1973
		FR 2148569 A	23-03-1973
		IT 961938 B	10-12-1973
		LU 65881 A	12-02-1973
		NL 7210946 A	13-02-1973
US 5368744 A	29-11-1994	AT 179999 T	15-05-1999
		DE 69418393 D	17-06-1999
		DE 69418393 T	28-10-1999
		EP 0637599 A	08-02-1995
		ES 2131161 T	16-07-1999
US 4835234 A	30-05-1989	CA 1326934 A	08-02-1994
		DE 3782222 A	19-11-1992
		DE 3782222 T	25-02-1993
		EP 0260108 A	16-03-1988
		EP 0464957 A	08-01-1992
US 5541252 A	30-07-1996	DE 4335567 A	20-04-1995
		AT 177449 T	15-03-1999
		CA 2152064 A	27-04-1995
		WO 9511269 A	27-04-1995
		DE 59407927 D	15-04-1999
		EP 0674678 A	04-10-1995
		ES 2130450 T	01-07-1999
		JP 8504885 T	28-05-1996
EP 0374478 A	27-06-1990	US 4956400 A	11-09-1990
		AT 155492 T	15-08-1997
		AT 190322 T	15-03-2000
		AT 190321 T	15-03-2000
		AU 613815 B	08-08-1991
		AU 4688889 A	21-06-1990
		BR 8906586 A	04-09-1990
		CA 2005668 A	19-06-1990
		CZ 8907166 A	14-10-1998
		DE 68928178 D	21-08-1997
		DE 68928178 T	05-02-1998
		DE 68929174 D	13-04-2000
		DE 68929175 D	13-04-2000
		EP 0763547 A	19-03-1997
		EP 0764661 A	26-03-1997
		EP 0763548 A	19-03-1997
		ES 2103704 T	01-10-1997
		GR 3026043 T	29-05-1998
		JP 2225502 A	07-09-1990
		JP 2744096 B	28-04-1998
		KR 154321 B	01-12-1998
		LT 1613 A,B	25-07-1995
		LV 11186 A	20-04-1996
		LV 11186 B	20-08-1996
		MX 18621 A	01-11-1993
		SK 716689 A	04-11-1998
		RU 2060258 C	20-05-1996
		RU 2056433 C	20-03-1996

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/01615

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0374478 A		RU 2056434 C	20-03-1996
		ZA 8909691 A	26-09-1990
		US 5037863 A	06-08-1991
<hr/>			

